This document contains Appendix D from the 2004 Holland America Oosterdam Data report. Appendix D contains Data Review Narratives and Other Issues concerning the Oosterdam, September 14 through September 24, 2004. The report and all the appendices for this sampling event can be downloaded from
http://www.epa.gov/owow/oceans/cruise_ships/oosterdam.html

Holland America Oosterdam

2004 Analytical Results

Appendix D

March 2006

Appendix D

DATA REVIEW NARRATIVES AND OTHER ISSUES

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6506

Data Validation Report For BOD_5 Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

February 10, 2005

BOD_5 Method 405.1

Completeness

During Sampling Episode 6506 aboard the HAL Oosterdam, a total of 33 samples (excluding QC samples) were collected for analysis of 5-day Biochemical Oxygen Demand (BOD_5) by EPA Method 405.1. Sample numbers ranged between 65792 and 66000. One sample from the food pulper vacuum tank could not be collected because this system was not operating during the sampling episode, resulting in a sampling completeness of 97% for this episode.

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete BOD_5 data for all submitted samples, resulting in a laboratory completeness of 100%. A list of samples collected and analyzed during Sampling Episode 6506 is provided in Table 1.

Table 1. BOD_5 Samples Collected During Sampling Episode 6506

Sample Numbers	Sample Point Description
65792	Accommodations Wastewater
65796	Laundry Wastewater
65800	Galley Wastewater
65808	Food Pulper Centrifuge
65812, 65816, 65820, 65824, 65828,	Influent to Graywater Treatment
65852, 65856, 65860, 65864, 65868, 65876, 65884	Effluent from Graywater Treatment
65896, 65900, 65904, 65908, 65912	Influent to Blackwater/Graywater Treatment
65936, 65940, 65944, 65948, 65952, 65968	Effluent from Blackwater/Graywater Treatment
65980, 65984, 65988, 65992, 65996	Final Combined Discharge
66000	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a minimum goal of 90% completeness for sampling and analytical completeness has been

established, and a minimum goal of 81% for overall completeness (determined by multiplying sampling and analytical completeness goals) has been established. For Sampling Episode 6506, overall completeness for BOD_5 was 97%.

Holding Times

Method 405.1 requires that all BOD_5 samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates all BOD_5 samples received by the laboratory were analyzed within the 48 hour holding time.

Calibration

The calibration of the BOD_5 test was performed with method blanks and glucose spiked blanks to verify seed effectiveness and analytical technique. Method blanks consist of potable water passed through an activated carbon bed to remove residual organic compounds. During Sampling Episode 6506, a total of three method blanks were prepared and analyzed for BOD_5. The results of the three method blank analysis showed BOD_5 concentrations less than 2 mg/L.

To verify seed effectiveness and analytical technique, method blanks were spiked with a sufficient amount of glucose to yield a theoretical BOD_5 concentration of 200 mg/L. Spiked method blanks are then analyzed for BOD_5 and results of the analysis, reported as percent recovery, are compared to the recovery limits for Method 405.1. Table 2 shows the results of the spiked samples. Results of the spike sample analyses indicate all recoveries are within the method-specified limits.

Table 2. Analysis of BOD_5 Recovery Data for Spiked Samples

Sample	Spike Result	Spike Level	Recovery	Recovery Limits
Method Blank	174 mg/L	200 mg/L	87%	60% - 140 %
Method Blank	169 mg/L	200 mg/L	84.5%	60% - 140%
Method Blank	166 mg/L	200 mg/L	83%	60% - 140%
Method Blank	172 mg/L	200 mg/L	86%	60% - 140%
Method Blank	183 mg/L	200 mg/L	91.5%	60% - 140%
Method Blank	176 mg/L	200 mg/L	88%	60% - 140%

Precision Analysis

Reproducibility for BOD_5 is measured as relative percent difference (RPD) between duplicate samples. Laboratory duplicate samples measure the precision of the method and analyst by comparing the results of two separate analyses of the same sample. Field duplicate samples measure the precision of the field sampling method by comparing the BOD_5 results for

split samples prepared in the field. The QAPP for the Cruse Ship Rulemaking provides RPD targets for all laboratory and field duplicate samples as less than 20% and 30%, respectively.

Table 3 shows the RPD results for duplicate method blank spiked samples and a laboratory duplicate sample. The RPDs shown in Table 3 indicate both the duplicate method blank spike samples and the laboratory duplicate samples are within the QAPP-specified RPD target of less than 20%.

Table 3. Relative Percent Difference Between Laboratory Duplicate Samples

Sample No.	BOD_5 Result	Duplicate BOD_5 Result	RPD	RPD Target
Spiked Method Blank	174 mg/L	169 mg/L	2.9%	<20%
Spiked Method Blank	166 mg/L	172 mg/L	3.6%	<20%
Spiked Method Blank	183 mg/L	176 mg/L	3.9%	<20%
65908	736 mg/L	824 mg/L	11.3%	<20%

RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

Table 4 shows the RPD results for field duplicate samples. All field duplicate samples are within the QAPP-specified target of less than 30%. The field data precision is acceptable and the BOD_5 results are valid.

Table 4. Relative Percent Difference Between Field Duplicate Samples

Sample No.	BOD_5 Result	Sample No.	BOD_5 Result	RPD	RPD Target
65856	25.9 mg/L	65876	29.4 mg/L	12.7%	<30%
65864	23.9 mg/L	65884	22.5 mg/L	6.0%	<30%
65948	4.42 mg/L	65968	3.9 mg/L	12.5%	<30%

RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.

Data Quality Assessment

This data validation assessment indicates all the BOD_5 data collected during Sampling Episode 6506 can be used for the large cruise ship rulemaking effort.

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MEMORANDUM

DATE: February 10, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Sara Clark, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Classical Analyses for the Alaskan Cruise Ship Industry (AKCS), Episode 6506

OVERVIEW

Under EPA Contract Number 68-C-03-058, ProChem (formerly QBioChem) submitted classical wet chemistry data for 37 aqueous samples and 4 solid samples in Episode 6506. Table 1 provides a listing of samples, matrices, descriptions, sampling dates and the required analytes.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates and Analytes

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65792	Aqueous	SP1, Accommodations	09/21/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65796	Aqueous	SP2, Laundry WW	09/19/04	
65800	Aqueous	SP3, Galley WW	09/20/04	
65808	Solid	SP5, Food pulper WW	09/22/04 (a), 09/23/04 (b)	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TOC, total cyanide
65812	Aqueous	SP6, Influent to GW TS	09/19/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65816	Aqueous	SP6, Influent to GW TS	09/20/04	
65820	Aqueous	SP6, Influent to GW TS	09/21/04	
65824	Aqueous	SP6, Influent to GW TS	09/22/04	
65828	Aqueous	SP6, Influent to GW TS	09/23/04	
65852	Aqueous	SP8, Effluent from GW TS	09/19/04	
65856	Aqueous	SP8, Effluent from GW TS	09/20/04	
65860	Aqueous	SP8, Effluent from GW TS	09/21/04	
65864	Aqueous	SP8, Effluent from GW TS	09/22/04	
65868	Aqueous	SP8, Effluent from GW TS	09/23/04	

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, Sampling Dates and Analytes

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65872	Aqueous	SP9, Effluent from GW TS	09/19/04	total cyanide
65880	Aqueous	SP9, Effluent from GW TS	09/22/04	alkalinity, chloride, sulfate, TDS, TSS, total cyanide
65884	Aqueous	SP9, Effluent from GW TS	09/22/04	ammonia-N, COD, nitrate/nitrite, total phosphorus, TKN, TOC
65888	Aqueous	SP9, Gray water effluent	09/23/04	
65896	Aqueous	SP11, Influent to BW/GW TS	09/19/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65900	Aqueous	SP11, Influent to BW/GW TS	09/20/04	
65904	Aqueous	SP11, Influent to BW/GW TS	09/21/04	
65908	Aqueous	SP11, Influent to BW/GW TS	09/22/04	
65912	Aqueous	SP11, Influent to BW GW TS	09/23/04	
65936	Aqueous	SP13, Effluent BW/GW TS	09/19/04	
65940	Aqueous	SP13, Blackwater effluent	09/20/04	
65944	Aqueous	SP13, Effluent BW/GW TS	09/21/04	
65948	Aqueous	SP13, Effluent BW/GW TS	09/22/04	
65952	Aqueous	SP13, Effluent from BW/GW TS	09/23/04	
65956	Aqueous	SP14, Effluent from BW/GW TS	09/19/04	total cyanide
65964	Aqueous	SP 14, Effluent from BW/GW TS	09/21/04	alkalinity, chloride, sulfate, TDS, TSS
65968	Aqueous	SP14, Effluent from BW/GW TS	09/22/04	ammonia-N, COD, nitrate/nitrite, total phosphorus, TKN, TOC
65972	Aqueous	SP14, Effluent from GW/GW TS	09/23/04	alkalinity, chloride, sulfate, TDS, TSS
65976	Solid	SP15, GW SWECO solids	09/20/04 (c), 9/21/04 (d)	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TOC, total cyanide

Table 1 - Sample Identifiers, Descriptions, Sampling Dates and Analytes

EPA Sample #	Matrix	Sample Description	Sampling Date	Analytes
65980	Aqueous	SP16, Final combined discharge	09/19/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide, HEM, SGT-HEM
65984	Aqueous	SP16, Combined discharge	09/20/04	
65988	Aqueous	SP16, Combined discharge	09/21/04	
65992	Aqueous	SP16, Combined discharge	09/22/04	
65996	Aqueous	SP16, Final combined discharge	09/23/04	
66000	Aqueous	SP17, Source water	09/20/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TDS, TSS, TOC, total cyanide
66009	Solid	SP20, BW/GW SWECO solids	09/21/04	alkalinity, ammonia-N, COD, chloride, nitrate/nitrite, sulfate, total phosphorus, TKN, TOC, total cyanide
66010	Solid	SP21, GW/BW Biosludge	09/21/04	

(a) Sampling date for total cyanide
(b) Sampling date for Group I and Group II
(c) Sampling date for Group II
(d) Sampling date for Group I and total cyanide

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004) and with the specifications listed in the contract. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the contract-specified holding times for all classical wet chemistry parameters specified in the sampling and analysis plan. The calibration and continuing calibration standards were successfully analyzed. Laboratory blanks were performed for each analysis, and there was no contamination detected above the laboratory reporting limits. The QC samples, including the ongoing precision and recovery sample (OPR) and matrix spike/matrix spike duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

DATA ISSUES: SGT-HEM

The OPR associated with samples 65828 and 65912 had spike recoveries that were below the acceptance limits specified by the method. Therefore, SCC considers the SGT-HEM data for these samples to be minimum values. This case is detailed in Table 2.

DATA ISSUES: AVAILABLE CYANIDE GREATER THAN TOTAL CYANIDE

Sample Results

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65896, 65900, 65904, 65908, and 65912, while total cyanide were not detected in these samples. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

A comparison of the total cyanide results and available cyanide results for samples 65896, 65900, 65904, 65908, and 65912 indicates that the total cyanide results were non-detects at 5 μg/L, while available cyanide was detected in each of these samples at levels from approximately 36 to 77 μg/L.

All five of these samples are from the same sampling point, SP 11, and represent influents to the black water and gray water treatment system. Thus, these samples are not treated effluents. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65896, 65900, 65904, 65908, and 65912 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6506, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

TECHNICAL NOTES:

Silica Gel Treated – Hexane Extractable Material (SGT-HEM)

Samples 65852, 65936, 65944, 65952, 65856, 65860, 65864, 65868, 65940, 65948, 65980, 65984, 65988, 65992 and 65996 were not analyzed for SGT-HEM because the HEM results were non-detects. At EPA's request, SCC created SGT-HEM records in the database, but the results for SGT-HEM are reported as NA, with the SCC qualifier reading "not analyzed due to non-detect HEM result."

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC
Pornkeo Chinyavong, CSC

Table 2
Data Review Summary Table

Episode: 6506 **Analysis:** Classicals

Industry: Alaska Cruise Ship **Reviewer:** Sara Clark

Sample	Analyte	Action	Reason	SCC Qual	Level
65896 65900 65904 65908 65912	total cyanide	Minimum value	Result for available cyanide greater than total cyanide	IRR	ND
65828	SGT-HEM	Minimum value	OPR was below acceptance limits	NA	ND
65912	SGT-HEM	Minimum value	OPR was below acceptance limits	NA	6 mg/L

ND = Non-detect at the laboratory's reporting limit. See the level in the database.
NA = Not applicable
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose

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MEMORANDUM

DATE: March 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Jody Donnelly, Quality Assurance Chemist JHD
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analysis for the Alaskan Cruise Ship Industry, Episode 6506

OVERVIEW

Under CSC Purchase Order 637415SSD, Axys Analytical Services submitted data for the analysis of dioxins and furans by EPA Method 1613B for one solid sample in Episode 6506. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6506	65892	Solid	SP10, Incinerator ash	09/22/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/Furan Analysis by Method 1613B (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable.

Reporting Limits

The sample was extracted using approximately 5 grams instead of the method-specified 10 grams. As a result, the minimum levels (MLs) provided in the database for sample 65892 increased by approximately a factor of 2. The laboratory's past experience with ash samples shows that they tend to have significant matrix interference, which is why the sample size was reduced. Because the laboratory calibrated their instrument to 5 times lower than the lowest calibration standard specified in Method 1613B, the difference in sample size has no impact on the quality of the data. The MLs provided in the database for these samples reflect the smaller sample size.

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Several analytes in sample 65892 were qualified by SCC with a “J” flag, which indicates an estimated result that is below the laboratory’s adjusted reporting limit but above the method detection limit. These analytes are annotated as such in the database and are detailed in Table 2.

If you have any questions regarding the analysis of this sample or the review of these data, please contact me, by telephone at (703) 461-2203 or by facsimile at (703) 461-8056.

Attachment

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6506 **Analysis:** Method 1613B

Industry: Alaskan Cruise Ship **Reviewer:** J. Donnelly

Sample	Analyte	Action	Reason	SCC Qual	Level (ng/kg)
65892	1,2,3,4,7,8-HxCDF	Estimated value	Analyte detected below laboratory's reporting limit but above method detection limit	J	5.20
	1,2,3,4,6,7,8-HpCDF				6.0
	OCDD				12.47

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MEMORANDUM

DATE: February 9, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Dioxin/Furan Analysis for the Alaskan Cruise Ship Industry, Episode 6506

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of dioxins and furans by EPA Method 1613B for one aqueous sample in Episode 6506. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifier, Description, Sampling Date, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6506	65796	Aqueous	SP2, Laundry Wastewater	9/19/04	1613B

These data have been reviewed in accordance with SCC's Data Review Guidelines for Dioxin/Furan Analysis by Method 1613B (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Method 1613B within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for the analysis detected no contamination above the laboratory's reporting limits. Instead of using the method-specified clean up procedure, all samples were processed by an automated clean up procedure that employs the Fluid Management System Inc., *"Power-Prep™ System,"* using standard chromatographic clean up columns. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable. No dioxins/furans were detected in the sample in this episode.

Reporting Limits

The sample was extracted using a 815-mL aliquot, rather than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the minimum levels (MLs) for sample 65796 by 23%. The MLs provided in the database for this sample reflect the smaller sample volume.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

If you have any questions regarding the analysis of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6506

Data Validation Report For Microbiological Analyses

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

February 10, 2005

Enterococci by MPN Method ASTM D6503-99
Fecal Coliform by MF SM 9222D
***E. Coli* by MPN Enzyme Substrate SM 9223B**

Completeness

During Sampling Episode 6506, a total of 111 samples (excluding QC samples) were collected for analysis of enterococci, fecal coliform, and *E. coli* by the methods listed above. Sample numbers ranged between 65792 and 66014. The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete microbiological data for all submitted samples. A list of the samples collected and analyzed during Sampling Episode 6506 is provided in Table 1.

Table 1. List of Samples and Required Microbiological Analyses for Sampling Episode 6506

Sample Numbers	Sample Point Description
65792	Accommodations Wastewater
65796	Laundry Wastewater
65801	Galley Wastewater
65808	Food Pulper Centrifuge
65812, 65813, 65816, 65817, 65820, 65821, 65824, 65825, 65828, 65829	Influent to Graywater Treatment
65832, 65833, 65834, 65836, 65837, 65838, 65840, 65841, 65842, 65844, 65845, 65846, 65848, 65849, 65850	Influent to Graywater Treatment UV Disinfection
65852, 65853, 65854, 65856, 65857, 65858, 65860, 65861, 65862, 65864, 65865, 65866, 65868, 65869, 65870, 65872, 65876, 65880, 66009, 66010, 66014	Effluent from Graywater Treatment
65896, 65897, 65900, 65901, 65904, 65905, 65908, 65909, 65912, 65913	Influent to Blackwater/Graywater Treatment
65916, 65917, 65918, 65920, 65921, 65922, 65924, 65925, 65926, 65928, 65929, 65930, 65932, 65933, 65934	Influent to Blackwater/Graywater Treatment UV Disinfection
65936, 65937, 65938, 65940, 65941, 65942, 65944, 65945, 65946, 65948, 65949, 65950, 65952, 65953, 65954, 65964, 65968, 65972, 66011, 66012, 66013	Effluent from Blackwater/Graywater Treatment

Sample Numbers	Sample Point Description
65980, 65981, 65984, 65985, 65986, 65988, 65989, 65990, 65992, 65993, 65994, 65996, 65997, 65998	Final Combined Discharge
66000	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a minimum goal of 90% completeness for sampling and analytical completeness has been established, and a minimum goal of 81% for overall completeness (determined by multiplying sampling and analytical completeness goals) has been established.

The number of microbiologicals samples actually collected onboard the Oosterdam increased from that described in the Oosterdam Sampling and Analysis Plan due to the collection of one sample from each of the graywater characterization sampling points (i.e., accommodations, laundry, galley, and food pulper centrifuge wastewater characterization) for analysis of each of the three microbiologicals. On the other hand, one grab sample was not collected on Sampling Day 1 at Sampling Point 16 (Final Combined Discharge) because the Oosterdam was not discharging wastewater while in State of Washington waters. As a result, sampling completeness was 103% for Sampling Episode 6506.

All collected samples were analyzed, and all results are valid, with the exception of one sample that was analyzed outside the holding time (see discussion under Holding Times below for additional information). Therefore, laboratory completeness was 99% and overall completeness was 102% for Sampling Episode 6506.

Holding Times

The QAPP developed for the cruise ship rulemaking requires all microbiological samples be analyzed within 6 hours following collection. Review of traffic reports and laboratory data sheets indicates microbiological Sample No. 65861 was not analyzed within the 6 hour hold time. Table 2 provides information regarding this sample.

Table 2. Microbiological Sample Exceeding Hold Times

Sample Number	Microbiological	Sample Hold Time	Method Hold Time	Result
65861	Fecal Coliform	28 hours	6 hours	<2 CFU/100mL
65861	Enterococci	28 hours	6 hours	<1 MPN/100mL

Sample Number	Microbiological	Sample Hold Time	Method Hold Time	Result
65861	*E. Coli*	28 hours	6 hours	<1 MPN/100mL

The sample, collected from gray water treatment system effluent, was analyzed approximately 28 hours after collection. Since the holding time for this sample was exceeded by approximately 22 hours, the data from this sample are not considered valid and will not be used for the cruise ship rulemaking. Accordingly, results for this sample will be excluded from the analytical database.

Detection Limits

Some microbiological results were reported by Analytica Alaska as "greater than" a specified value (e.g., >2,240 MPN/100 mL). These results are qualified in the analytical database by a ">" flag and are listed in Table 3. This qualifier indicates the sample was not diluted sufficiently (i.e., the measured concentration exceeds the range of dilutions). The reported results in the database are the upper limit of the measurement range, and the ">" flag indicates that the actual concentrations are some level greater than the reported upper limit. Although the results are valid, data users should consider this data qualification in using the data.

Table 3. Microbiological Sample Results with ">" Qualifier

Analysis	Sample Numbers
Enterococci	65813, 65926

Calculation of Fecal Coliform Density

Fecal coliform density should be computed from sample quantities that produced membrane filtration counts within the desired range of 20 to 60 fecal coliform colonies. This was not always possible for many cruise vessel samples for various reasons. First, many samples, such as wastewater treatment effluent samples, had low concentrations of microbiological contaminants, and the occurrence of fecal coliform colonies was minimal. In these cases, as specified by the method, the analyst counted all fecal coliform colonies, disregarding the lower limit of 20.

Second, most samples (other than wastewater treatment effluent) required a series of sample dilutions to obtain between 20 and 60 colony forming units per filter pad. In most cases, the analyst obtained a result within this range using one of the prepared dilutions. However, in a few instances, no single filter generated a result within the desired range (i.e., two results within the desired range, two results either above or below the desired range, one result above and one result below the desired range, etc). In these cases, as specified by the method, the analyst totaled the counts on the two filters and reported the result as a number per 100 mL. Table 4 lists the fecal coliform samples for Sampling Episode 6506 that did not yield a single result

within the desired range, and for which the analyst computed the number of colony forming units based on a calculation of the results from multiple plates. Calculations for these samples are provided in the Cruise Ship Rulemaking Record.

Table 4. Fecal Coliform Samples For Which Multiple Plates Were Used to Compute CFU/mL

Sample Number	Sample Description
65792	Accommodations Wastewater
65816, 65824, 65828	Influent to Graywater Treatment
65837, 65840, 65841, 65844, 65848, 65849	Influent to Graywater Treatment System UV Disinfection
65900, 65901, 65905	Influent to Blackwater/Graywater Treatment System
65916, 65920, 65921, 65925, 65930	Influent to Blackwater/Graywater Treatment System UV Disinfection

In summary, calculation of fecal coliform density was performed as specified by the method, and the reported results are valid.

Laboratory QC Measures

QC measures for microbiologicals include positive and negative controls, media sterility checks, dilution water sterility checks, sample bottle blanks, membrane filter preparation blanks, and verification of incubator temperatures. The following describes the results of each of these QC checks used during Sampling Episode 6506. (The actual QC results are contained in Analytica Alaska's laboratory report, which is provided in the Cruise Ship Rulemaking Record.)

Positive and Negative Controls

Positive and negative controls are known cultures that are analyzed exactly like the field samples, and will produce an expected positive or negative result for a given type of medium. For Sampling Episode 6506, one medium-specific positive and negative control was analyzed for each medium lot used. Results of the positive and negative controls indicate the media used by the field laboratory for Sampling Episode 6506 produced expected results.

Media Sterility Checks

Media are checked for sterility by incubating the media at the appropriate temperature without sample and observed for growth. For Sampling Episode 6506, one medium sterility check was performed for each medium lot used. The media sterility check verified the media

used by the field laboratory had not been contaminated with any of the microorganisms being analyzed for this work.

Dilution Water Sterility Checks

Dilution water is analyzed exactly like a field sample and observed for growth of fecal coliform, *E. coli*, and enterococci to verify the water is not contaminated with these organisms prior to use. For Sampling Episode 6506, one sample dilution blank was analyzed for each lot of dilution water used. Results of dilution water blank analysis verified the water had not been contaminated with any of the microorganisms being analyzed for this work.

Sample Bottle Blank

A sample bottle blank was analyzed for each bottle lot used during Sampling Episode 6506 to determine adequate bottle sterilization prior to use by the sampling crew. Results of the sample bottle blank (dilution water poured into the sample bottle and analyzed) verified the sample bottles had not been contaminated with any of the microorganisms being analyzed for this work.

Membrane Filter Preparation Blank

Membrane filter blanks were analyzed at the beginning of each set of filtered samples to document adequate sterilization of membrane filtration equipment. Membrane blanks verified that the equipment used for filtration during Sampling Episode 6506 had not been contaminated with any of the microorganisms being analyzed for this work.

Incubator Temperature

Incubator temperatures were monitored in the onboard laboratory to verify that prepared microbiological samples were being incubated at the correct temperatures. Review of the laboratories incubator log sheets generated during Sampling Episode 6506 verified the temperature was measured and recorded twice daily, no less than four hours apart, and the temperature checks were ± 0.5°C apart.

Precision Analysis

Reproducibility for the microbiological analyses is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking presents the target RPD for all laboratory and field duplicate samples as less than 20% and 30%, respectively. During Sampling Episode 6506, additional 100-ml sample volumes were collected for a number of grab samples with the intent that the laboratory would prepare a single composite and then analyze duplicate samples from the composite to evaluate laboratory precision (i.e., laboratory duplicates). The laboratory did not prepare a composite, but instead analyzed each of the 100-ml sample volumes individually. Because a composite was not

prepared, laboratory precision could not be evaluated. The results obtained from analysis of these individual sample volumes are field duplicates, not laboratory duplicates, and because they were collected as laboratory duplicates, the original sample and the duplicate sample have the same sample number. In order to differentiate the original from the duplicate, ERG assigned new SCC numbers (66009, 66010, 66011, 66012, 66013, and 66014) to the duplicate samples.

During Sampling Episode 6506, six additional sets of intended field duplicate samples (i.e., different sample numbers) were also collected and analyzed by each of the three microbiological methods. These field duplicate samples were prepared to determine the precision of the field sampling equipment. Duplicate sample data for the samples described above, along with the six intended field duplicate samples, are provided for *E. coli*, fecal coliform, and enterococci in Tables 5, 6, and 7.

Table 5. *E. Coli* Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65852	65872	ND	ND	NA	<30%
65856	65876	ND	ND	NA	<30%
65860	65880	ND	ND	NA	<30%
65944	65964	ND	ND	NA	<30%
65948	65968	ND	ND	NA	<30%
65952	65972	ND	ND	NA	<30%
65852	66014*	ND	ND	NA	<30%
65856	66015*	ND	ND	NA	<30%
65860	66016*	ND	ND	NA	<30%
65944	66011*	ND	ND	NA	<30%
65948	66012*	ND	ND	NA	<30%
65952	66013*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 or 2 MPN/100 mL.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 6. Fecal Coliform Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65852	65872	ND	ND	NA	<30%
65856	65876	1.0 CFU/100ml	1.0 CFU/100ml	0%	<30%
65860	65880	ND	ND	NA	<30%
65944	65964	ND	ND	NA	<30%
65948	65968	ND	ND	NA	<30%
65952	65972	ND	ND	NA	<30%
65852	66014*	ND	ND	NA	<30%
65856	66015*	1.0 CFU/100ml	1.0 CFU/100ml	0%	<30%
65860	66016*	ND	2.0 CFU/100ml	NA	<30%
65944	66011*	ND	ND	NA	<30%
65948	66012*	ND	ND	NA	<30%
65952	66013*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 or 2 CFU/100ml.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

Table 7. Enterococci Results for Duplicate Samples

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65852	65872	ND	ND	NA	<30%
65856	65876	ND	ND	NA	<30%
65860	65880	ND	ND	NA	<30%
65944	65964	ND	ND	NA	<30%
65948	65968	ND	ND	NA	<30%
65952	65972	ND	ND	NA	<30%
65852	66014*	ND	ND	NA	<30%
65856	66015*	ND	ND	NA	<30%
65860	66010*	ND	ND	NA	<30%

Sample No.	Dup Sample No.	Sample Result	Dup Sample Result	RPD	Target RPD
65944	66011*	ND	ND	NA	<30%
65948	66012*	ND	ND	NA	<30%
65952	66013*	ND	ND	NA	<30%

NA: RPD can not be calculated since one or both of the sample results is less than the laboratory reporting limit.
ND: Measured concentration less than the laboratory reporting limit of 1 MPN/100 mL.
Target RPD from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004.
*SCC numbers were fabricated to distinguish original sample from intended laboratory duplicate.

The data provided in Tables 5, 6, and 7 show that nearly all of the field duplicate samples analyzed by the laboratory gave nearly the same measured values. All the duplicate sample sets either had RPDs within the QAPP-specified target of 30%, or the RPDs could not be calculated because one or both of the duplicate sample results was less than the laboratory reporting limit. Based on the duplicate sample results provided in Tables 5, 6 and 7, the microbiological analysis precision is acceptable for this program, and the reported microbiological results are valid.

Data Quality Assessment

This data validation assessment indicates the microbiological data collected during Sampling Episode 6506 can be used for the large cruise ship rulemaking effort, with the exception of results for sample 65861, which was analyzed outside the 6-hour holding time.

Data users should consider limitations of sample results derived from overly low sample dilution (identified with a “>” flag) as they use the data.

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MEMORANDUM

DATE: February 11, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Julie Dixon Rest, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Total and Dissolved Metals Analyses for the Alaska Cruise Ship Industry Project, Episode 6506

OVERVIEW

Under EPA contract number 68-C-03-044, ProChem Analytical (formerly Q BioChem), submitted data for total and dissolved metals by EPA Methods 200.7, 200.9, 245.1, and 245.5 in Episode 6506. The thirty-three aqueous samples and five solid samples in this episode were analyzed for twenty-five metals by Method 200.7 (ICP-AES) and for thallium by Method 200.9 (GFAA). Mercury analyses of the aqueous samples were performed by Method 245.1, and by Method 245.5 for the solid samples. Table 1 provides a list of samples, matrices, sampling dates, and the required analytical methods.

All thirty-three aqueous samples were analyzed for total and dissolved metals. The five solid samples were analyzed for total metals. The laboratory added the suffixes "D" and "T" to the sample numbers on the hard copy results to differentiate the analyses for dissolved metals and total metals, respectively. These suffixes are also used in this data review narrative. However, the sample numbers in the database will not contain these suffixes. Consistent with current EAD protocols, the total and dissolved metals distinctions are provided in the "procedure" field of the database.

This episode included data for three matrix spike/matrix spike duplicate MS/MSD pairs for aqueous effluent samples. Of these, all three were analyzed for total and dissolved metals.

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65792	Aqueous	SP1, Accommodations wastewater	9/21/04	200.7, 200.9, and 245.1
65796	Aqueous	SP2, Laundry wastewater	9/19/04	
65800	Aqueous	SP3, Galley wastewater	9/20/04	
65808	Solid	SP5, Food pulper	9/23/04	200.7, 200.9, and 245.5
65812	Aqueous	SP6, Gray water influent	9/19/04	200.7, 200.9, and 245.1
65816	Aqueous	SP6, Gray water influent	9/20/04	
65820	Aqueous	SP6, Gray water influent	9/20/04	
65824	Aqueous	SP6, Gray water influent	9/22/04	

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65828	Aqueous	SP6, Gray water influent	9/23/04	200.7, 200.9 and 245.1
65852	Aqueous	SP8, Gray water effluent	9/19/04	
65856	Aqueous	SP8, Gray water effluent	9/20/04	
65860	Aqueous	SP8, Gray water effluent	9/21/04	
65864	Aqueous	SP8, Gray water effluent	9/22/04	
65868	Aqueous	SP8, Gray water effluent	9/23/04	
65880	Aqueous	SP9, Gray water effluent, duplicate	9/21/04	
65892	Solid	SP10, Incinerator ash	9/22/04	200.7, 200.9 and 245.5
65896	Aqueous	SP11, Influent to BW/GW treatment	9/19/04	200.7, 200.9 and 245.1
65900	Aqueous	SP11, Influent to BW/GW treatment	9/20/04	
65904	Aqueous	SP11, Influent to BW/GW treatment	9/21/04	
65908	Aqueous	SP11, Influent to GW/BW TS	9/22/04	
65912	Aqueous	SP11, BW/CW influent	9/23/04	
65936	Aqueous	SP13, Effluent BW/GW treatment	9/19/04	
65940	Aqueous	SP13, Black water effluent	9/20/04	
65944	Aqueous	SP13,Effluent BW/GW treatment	9/21/04	
65948	Aqueous	SP13, Effluent BW/GW treatment	9/22/04	
65952	Aqueous	SP13, Effluent BW/GW treatment	9/20/04	
65956	Aqueous	SP14, Effluent BW/GW treatment	9/19/04	
65964	Aqueous	SP14, Effluent BW/GW treatment	9/19/04	
65976	Solid	SP15, GWTS SWECO solids	9/20/04	200.7, 200.9 and 245.5
65980	Aqueous	SP16, Combined discharge	9/19/04	200.7, 200.9 and 245.1
65984	Aqueous	SP16, Combined discharge	9/19/04	
65988	Aqueous	SP16, Combined discharge	9/19/04	
65992	Aqueous	SP16, Combined discharge	9/22/04	
65996	Aqueous	SP16, Final effluent	9/23/04	
66000	Aqueous	SP17, Source water	9/19/04	
66008	Aqueous	SP19, Equipment blank	9/19/04	
66009	Solid	SP20, BW/GW TS solids	9/21/04	200.7, 200.9 and 245.5
66010	Solid	SP21, BW/GWTS biosludge	9/21/04	

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Metals Analyses for Tasks I and II Metals Analysis* (November 2004) and with the specifications listed in EPA Method 200.7 (Rev. 5), 200.9 (Rev. 2.2), and 245.1(03/83), and 245.5(03/83). All data are of acceptable quality with the qualifiers described below and detailed in the data review summary table (Table 2).

SUMMARY

All 38 samples were successfully analyzed within the specified holding times. The initial precision and recovery (IPR) analyses and the method detection limit (MDL) study were performed and met the specified criteria. Calibration curves, calibration standards, and calibration blanks were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory reporting limits, with the exceptions noted below and detailed in Table 2. QC samples, including laboratory control sample (LCS), matrix spike (MS) sample, matrix duplicate (MSD) sample, and laboratory serial dilution sample demonstrated that laboratory performance for these analyses was acceptable, with the exception of the issues described below.

DATA ISSUES:

Preparation and Continuing Calibration Blanks

Several elements were detected in the preparation blanks and some of the continuing calibration blanks (CCBs) associated with the samples in this episode at concentrations greater than the respective MDLs, but less than the method-specified MLs. (Note: This is a function of the change in reporting limits requested by EPA after the fact and not an issue of laboratory performance.) The data quality is affected as follows:

- Sample Results Less than Five Times Blank Results: When the sample result is less than five times the blank result, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Therefore, SCC recommends that the data for these analytes be reported in the database as non-detects at the minimum level, adjusted for dilution. These instances are detailed in the attached Data Review Summary Table (Table 2).

- Sample Results Greater than Five Times but Less than Ten Times Blank Results: SCC considers these data to be of acceptable quality but cautions the data user that the results may represent maximum values. This instance is detailed in Table 2.

- Sample Results Greater than Ten Times Blank Results or Analyte Not Detected in Sample: SCC does not consider the presence of the analyte in the blank to adversely affect the data in cases where the sample results are greater than ten times the associated blank results or where the analyte is not detected in associated samples.

Serial Dilutions

Serial dilutions were performed on samples 65880, 65964 and 65956. For copper in sample 65956, the percent difference (%D) between the original sample and the dilution exceeded the method-specified criteria. Therefore, SCC considers the sample result for Cu in sample 65956 to be an estimated value.

TECHNICAL NOTES

For the ICP analytical analyses for aqueous samples, thirteen analyses (10 samples and 3 QC samples) were performed between continuing calibration (CCV) and blank (CCB) checks. Since the CCV/CCB acceptance criteria were met, the data are considered acceptable without qualification.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachment

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodie King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2
Data Review Summary Table

Episode: 6506 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Solid 65976, 65808	B	Report in database as non-detect	Sample results <5x blank result	NA	ND
Solid 65976, 65808	Sn	Report in database as non-detect	Sample results <5x blank result	NA	ND
Solid 66009	Sn	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Solid 65808, 65976 66009, 66010	Co	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 65852, 65856, 65860, 65864, 65868, 65980, 65984, 65988, 65992	Al	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 65800, 65936, 65940, 65944, 65948, 65956, 65964, 65996	Al	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Dissolved 65828, 65864, 65868, 65904, 65908, 65912, 65944, 65948, 65952, 65964, 65996	B	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 65988, 65992	B	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Dissolved 65860, 65864, 65880, 66008	Ca	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 65796, 65852, 65856	Ca	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Dissolved 65860, 65880	Mg	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 65852, 65856	Mg	Maximum value	Sample results < 5x and >10x blank result	NA	See database report

Table 2
Data Review Summary Table

Episode: 6506 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Dissolved 66008	Mn	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 65864	Ni	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 66008	Zn	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 66000	Zn	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Total 65852, 65856, 65860, 65880, 65980, 65984, 66000, 66008	Al	Report in database as non-detect	Sample results <5x blank result	NA	ND
Total 65800, 65936, 65940, 65956	Al	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Total 65812, 65816, 65820, 65824, 65852, 65856, 65860, 65880, 65896, 65900, 65936, 65940, 65956, 65984	B	Report in database as non-detect	Sample results <5x blank result	NA	ND
Total 65792, 65800, 65796, 65980	B	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Total 65864	Ca	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Total 66008	Na	Report in database as non-detect	Sample results <5x blank result	NA	ND
Total 65796, 65856, 65980, 65984	Pb	Report in database as non-detect	Sample results <5x blank result	NA	ND
Total 65812, 65852, 65940	Pb	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Total 65824, 65956	Sb	Report in database as non-detect	Sample results <5x blank result	NA	ND

Table 2
Data Review Summary Table

Episode: 6506 **Analysis:** Metals

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
Total 65828, 65912	V	Report in database as non-detect	Sample results <5x blank result	NA	ND
Dissolved 66000	Zn	Maximum value	Sample results < 5x and >10x blank result	NA	See database report
Total 65956	Cu	Estimated value	%D for serial dilution exceeded criteria	NA	51.7 µg/L

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MEMORANDUM

DATE: February 11, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Julie Rest, Quality Assurance Chemist JDR
Sample Control Center

SUBJECT: Data Review Narrative for Organics Analyses for the Alaskan Cruise Ship Industry, Episode 6506

OVERVIEW

Under EPA Contract Number 68-C-03-033, Ecology and Environmental (E&E) submitted data for analysis of volatiles by Method 624 and for semivolatile organics by Method 625 in Episode 6506. Table 1 provides a listing of samples, sample descriptions, matrices, sampling dates, and the required analytical methods. This episode included thirty-three aqueous samples and four solid samples for Method 624 analysis and thirty-five aqueous samples and five solid samples for Method 625 analysis. The package included data for four matrix spike (MS) and matrix spike duplicate (MSD) pairs for Method 624 analysis, and four MS/MSD pairs for Method 625 analysis.

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65792	Aqueous	SP1, Accommodations wastewater	9/21/04	624, 625
65796	Aqueous	SP2, Laundry wastewater	9/19/04	
65800	Aqueous	SP3, Galley wastewater	9/20/04	
65808	Solid	SP5, Food pulper	9/22/04	
65812	Aqueous	SP6, Gray water influent	9/19/04	
65816	Aqueous	SP6, Gray water influent	9/20/04	
65820	Aqueous	SP6, Gray water influent	9/21/04	
65824	Aqueous	SP6, Gray water influent	9/22/04	
65828	Aqueous	SP6, Gray water influent	9/23/04	
65852	Aqueous	SP8, Gray water effluent	9/19/04	
65856	Aqueous	SP8, Gray water effluent	9/20/04	
65860	Aqueous	SP8, Gray water effluent	9/21/04	624, 625
65864	Aqueous	SP8, Gray water effluent	9/22/04	
65868	Aqueous	SP8, Gray water effluent	9/23/04	
65872	Aqueous	SP9,Gray water effluent, duplicate	9/19/04	625
65876	Aqueous	SP9, Gray water effluent, duplicate	9/20/04	624, 625

Federal Sector
Civil Systems Development Division
6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Descriptions, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Methods
65892	Solid	SP10, Incinerator ash	9/22/04	625
65896	Aqueous	SP11, Influent to BW/GW treatment	9/19/04	624, 625
65900	Aqueous	SP11, Influent to BW/GW treatment	9/20/04	
65904	Aqueous	SP11, Influent to BW/GW treatment	9/21/04	624, 625
65908	Aqueous	SP11, Influent to GW/BW TS	9/22/04	
65912	Aqueous	SP11, BW/CW influent	9/23/04	
65936	Aqueous	SP13, Effluent BW/GW treatment	9/19/04	
65940	Aqueous	SP13, Black water effluent	9/20/04	
65944	Aqueous	SP13,Effluent BW/GW treatment	9/21/04	
65948	Aqueous	SP13, Effluent BW/GW treatment	9/22/04	
65952	Aqueous	SP13, Effluent BW/GW treatment	9/23/04	
65960	Aqueous	SP14, BW Effluent, duplicate	9/20/04	
65968	Aqueous	SP14, Effluent BW/GW treatment	9/23/04	
65976	Solid	SP15, GWTS SWECO solids	9/21/04	
65980	Aqueous	SP16, Combined discharge	9/19/04	
65984	Aqueous	SP16, Combined discharge	9/20/04	
65988	Aqueous	SP16, Combined discharge	9/21/04	
65992	Aqueous	SP16, Combined discharge	9/22/04	
65996	Aqueous	SP16, Final effluent	9/23/04	
66000	Aqueous	SP17, Source water	9/20/04	624, 625
66004	Aqueous	Trip blank	9/22/04	624
66008	Aqueous	SP19, Equipment blank	9/19/04	625
66009	Solid	SP20, BW/GW TS solids	9/21/04	624, 625
66010	Solid	SP21, BW/GWTS biosludge	9/21/04	

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Volatile and Semivolatile Analysis by Methods 624 and 625* (November 2004) and according to the specifications in the methods. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached Tables 2A and 2B.

SUMMARY

All samples were successfully analyzed for the target analytes according to EPA Methods 624 and 625. Method 625 samples were extracted and analyzed within the method-specified holding times with the exception of those detailed below. Method 624 samples were prepared and analyzed within holding times with the exception of those noted below. GPC cleanup was performed on selected samples. All calibration and continuing calibration standards were successfully analyzed. Preparation blanks

performed for each analysis detected no contamination above the laboratory reporting limits. The QC samples, including the ongoing precision and recovery samples (OPR), and MS/MSD samples; as well as surrogate and internal standard recoveries, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below.

Multiple Qualifiers

Some of the analytical results were affected by multiple qualifiers. In cases where these qualifiers suggest different biases, SCC considers the data to be estimated values. The effect of each QC failure and its associated qualifier is described in the data review narrative. Where multiple qualifiers occur, the cumulative effects of the associated qualifiers are documented in the attached Tables 2A and 2B.

DATA ISSUES: METHOD 624

Surrogate Recoveries

One or more surrogate recoveries were above the acceptance criteria for solid samples 65808, 65976, 66009, and 66010. In addition, samples 65808 and 65976 had percent recoveries that were below criteria for one or more of the internal standards. The samples were reanalyzed with similar recoveries, indicating a matrix effect. When surrogate recoveries are above th acceptance criteria, the detected results in the sample are considered to be maximum values, and non-detected results are considered unaffected. However, when combined with low internal standard recoveries, as is the case for samples 65808 and 65976, SCC considers detected results to be estimated values. These instances are detailed in Table 2A.

Holding Times

As noted in the laboratory narrative, samples 65960, 65960MS, 65960MSD, and 66000 were analyzed approximately 8 hours after the holding time had expired, due to an instrument malfunction during the original analysis attempt. Therefore, SCC considers the results for samples 65960 and 66000 to be minimum values. These instances are detailed in Table 2A.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

MS/MSDs were prepared for aqueous samples 65876, 65960, and 65968. For sample 65876, chloroethane, trichlorofluoromethane, and 1,1-dichloroethene were recovered above the acceptance criteria in the MS, and trichlorofluoromethane, and 1,1-dichloroethene were recovered above the acceptance criteria in the MSD. When MS/MSD recoveries are above the acceptance criteria, the detected results in the sample are considered to be maximum values. Non-detected results are not affected by the high recoveries. Since these analytes were not detected in the unspiked sample, SCC considers the data to be acceptable without qualification.

2-Chloroethyl vinyl ether was not recovered in the MS/MSD samples prepared for samples 65876 and 65960. Although Method 624 does not provide QC limits for the recoveries, the lack of recoveries in the MS/MSD indicate potential difficulties in the analysis of this compound in samples. Therefore, SCC recommends excluding 2-chloroethyl vinyl ether result for samples 65876 and 65960 from the analytical database.

2-Chloroethyl vinyl ether was recovered below the acceptance criteria in the MS/MSDs prepared for aqueous sample 65968 and solid sample 66009. Therefore, SCC considers the non-detected results for this compound in samples 65968 and 66009 to be minimum values.

1,1-Dichloroethene was recovered above the acceptance criteria in the MS/MSD prepared for sample 65968. When MS/MSD recoveries are above method criteria, non-detected results in the unspiked sample are not affected. Therefore, SCC considers the results for 1,1-dichloroethene in sample 65968 to be acceptable without qualification.

DATA ISSUES: METHOD 625

Surrogate Recoveries

For samples 65896, 65900, 65904, 65908, and 65996, the recovery for surrogate 2-fluorophenol was below the acceptance criteria. In instances where one or more of the surrogates exceed criteria, SCC considers the extraction process to be in control based on the acceptable recovery of the remaining surrogates and on acceptable internal standard recoveries.

All surrogate recoveries were below the acceptance criteria in the neat analysis of sample 66010, indicating a matrix effect. The sample was reanalyzed at a ten-fold dilution, due to a high concentration of phenol and, again, all surrogate recoveries were below criteria. Therefore, SCC considers results for all analytes in sample 66010 to be minimum values.

For solid sample 65892, the recovery for surrogate 2,4,6,-tribromophenol was below the acceptance criteria. However, since all other surrogate recoveries and internal standard recoveries were acceptable, SCC considers the data to be acceptable without qualification.

Holding Times

As noted in the laboratory narrative, samples 65792, 65820, 65824, 65828, 65904, 65908, 65912, and 66010 were extracted 9 days after the holding time had expired, due to spiking problems in the initial extraction batch. Therefore, SCC considers all results in these samples to be minimum values. These instances are detailed in Table 2B.

Blanks

Bis (2-ethylhexyl) phthalate was detected in the preparation blank associated with samples 65792, 65820, 65824, 65828, 65904, 65908, 65912, and 66010, at a level greater than the MDL, but less than the method-specified ML. The data quality is affected as follows:

- Sample Results Less than Five Times Blank Results: When the sample result is less than five times the blank result, there are no means by which to ascertain whether or not the presence of the analyte may be attributed to contamination. Therefore, SCC recommends that the data be reported in the database as a non-detect at the ML, adjusted sample size and dilution. These instances included bis(2-ethylhexyl) phthalate in four samples as detailed in Table 2B.

- Sample Results Greater than Five Times but Less than Ten Times Blank Results: SCC considers these results to be of acceptable quality, but they may be maximum values. These instances included bis(2-ethylhexyl) phthalate in four samples as detailed in Table 2B.

- Sample Results Greater than Ten Times Blank Results or Analyte Not Detected in Sample: SCC does not consider the presence of the analyte in the blank to adversely affect the data in cases where the sample results are greater than ten times the associated blank results or where the analyte is not detected in associated samples. Because SCC considers such data to be acceptable without qualification, these cases do not merit further detail.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

MS/MSD samples were prepared for aqueous samples 65872, 65876, and 65960, and for solid sample 66009. A few analytes in the aqueous MS/MSDs had recoveries that were above the acceptance criteria and relative percent differences (RPDs) between the MS and MSD that exceeded criteria. In addition, two analytes were not recovered in the solid MS and/or MSD. When recoveries are above the acceptance criteria, the detected result for that analyte in the unspiked sample is considered to be a maximum value. For RPD failures, or when percent recovery failures are combined with RPD failure, SCC considers detected results in the unspiked samples to be estimated values. As a result, all analytes with the exception of phenol in samples 65872 and 65960 were acceptable without qualification. Analytes not recovered in the MS/MSD for solid sample 65960 are excluded from the analytical database for the unspiked sample. These instances are detailed in Table 2B.

Ongoing Precision and Recovery (OPR)

Due to laboratory oversight, the spiking solution used by the laboratory for one of the three OPRs prepared for this episode contained an abbreviated list of target compounds. The other three OPRs contained the full compound list. Since all OPR percent recoveries were acceptable, SCC believes that the laboratory performance is in control and that the sample data are not affected by this omission.

TECHNICAL NOTES:

Analysis of "1,2", "1,3", and "1,4"-Dichlorobenzene

Due to the nature of the dichlorobenzenes, (1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene), these compounds may be analyzed by either Method 624 or Method 625. For this episode the laboratory reported the sample results for these analytes by both methods. All sample results were non-detects. Because Method 625 is the more common method associated with the dichlorobenzenes and in order to maintain consistency in the analytical database, SCC has included only the sample results from Method 625 in the database.

Target Analyte List

Due to the large number of analytes that may be detected using these methods, the target compound lists for Methods 624 and 625 may vary slightly depending on the laboratory performing the analysis. For Episode 6506, the target analyte list differs from Episode 6503, in that it does not include the following analytes: benzidine, hexachlorocyclopentadiene, N-nitrosodiphenylamine, and N-nitrosodimethylamine.

Reporting Limits

The reporting limits requested for this project are the same limits required for Methods 1624 and 1625. For Method 624, however, the laboratory reported levels lower than those required for Method 1624. The laboratory limits for both methods, however, reflect the lowest initial calibration (ICAL) standard, adjusted for sample size and dilution.

Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency in the database, all "J" flagged data will be reported in the database as non-detects at the MLs as specified in Method 1624 and 1625, as required for this project.

Percent Solids Determination

According to the laboratory narrative, sample 65808 erupted from the vial when the cap was removed and, as a result, the laboratory did not perform the percent solids analysis on this sample. The sample results and reporting limits used by the laboratory are based on wet weight. Percent solids results determined by the classicals laboratory for this sample are provided in the analytical database.

Sample Results

Sample 66010 was analyzed as a solid sample for the Method 624 analysis and as an aqueous sample for the Method 625 analysis. Due to the low percent solids in this sample, the results and reporting limits for the Method 624 analysis are based on wet weight. Percent solids results determined by the classicals laboratory for this sample are provided in the analytical database.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's data review team leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2A
Data Review Summary Table

Episode: 6506 **Analysis:** Method 624

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
65976	chloroform	Estimated value	High surrogate standard recoveries; low internal standard recoveries	NA	24 µg/kg
65976	toluene	Estimated value	High surrogate standard recoveries; low internal standard recoveries	NA	80 µg/kg
65976	ethyl benzene	Estimated value	High surrogate standard recoveries; low internal standard recoveries	NA	55 µg/kg
65960	All 624 analytes	Minimum values	Analytical holding time exceeded	NA	ND
66000	All 624 analytes except chloroform	Minimum values	Analytical holding time exceeded	NA	ND
66000	chloroform	Minimum value	Analytical holding time exceeded	NA	24 µg/L
66009	toluene	Maximum value	High surrogate standard recoveries	NA	530 µg/kg
65968, 66009	2-chloroethyl vinyl ether	Minimum value	Low MS/MSD recoveries	NA	ND
65876, 65960	2-chloroethyl vinyl ether	Exclude	0% recoveries in the MS/MSDs	Exclude	NA

Table 2B
Data Review Summary Table

Episode: 6506 **Analysis:** Method 625

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
66010	All 625 analytes except phenol	Minimum values	Low surrogate recoveries; extraction holding time exceeded	NA	ND
66010	phenol	Minimum values	Low surrogate recoveries; extraction holding time exceeded	NA	380 µg/L
65792	phenol	Minimum value	Extraction holding time exceeded	NA	62 µg/L
65792, 65820, 65824, 65828	bis (2-ethylhexyl) phthalate	Report as non-detect; Minimum value	Sample result <5x blank result; extraction holding time exceeded	NA	ND
65820	phenol	Minimum value	Extraction holding time exceeded	NA	62 µg/L
65792, 65820, 65824, 65828, 65904, 65908, 65912	All 625 analytes except those mentioned elsewhere in this narrative	Minimum values	Extraction holding time exceeded	NA	ND
65820	diethyl phthalate	Minimum value	Extraction holding time exceeded	NA	14 µg/L
65824	phenol	Minimum value	Extraction holding time exceeded	NA	51 µg/L
65824	diethyl phthalate	Minimum value	Extraction holding time exceeded	NA	12 µg/L
65828	phenol	Minimum value	Extraction holding time exceeded	NA	32 µg/L
65828	diethyl phthalate	Minimum value	Extraction holding time exceeded	NA	12 µg/L
65904	phenol	Minimum value	Extraction holding time exceeded	NA	60 µg/L
65904	bis (2-ethylhexyl) phthalate	Estimated value	Sample result > 5x but <10x blank result; extraction holding time exceeded	NA	45 µg/L
65908	phenol	Minimum value	Extraction holding time exceeded	NA	100 µg/L

Table 2B
Data Review Summary Table

Episode: 6506 **Analysis:** Method 625

Industry: Alaskan Cruise Ship **Reviewer:** J. Rest

Sample	Analyte	Action	Reason	SCC Qual	Level
65908	bis (2-ethylhexyl) phthalate	Estimated value	Sample result > 5x but <10x blank result; extraction holding time exceeded	NA	47 µg/L
65912	bis (2-ethylhexyl) phthalate	Estimated value	Sample result > 5x but <10x blank result; extraction holding time exceeded	NA	47 µg/L
65912	phenol	Minimum value	Extraction holding time exceeded	NA	150 µg/L
65872	phenol	Estimated value	RPD between MS and MSD exceeds criteria	NA	65 µg/L
65960	3,3'-dichlorobenzidine 4-nitrophenol	Exclude	0% recoveries in the MS and/or MSD	Exclude	NA
65960	phenol	Estimated value	RPD between MS and MSD exceeds criteria	NA	60 µg/L
66010	bis (2-ethylhexyl) phthalate	Estimated value	Sample result > 5x but <10x blank result; low surrogate recoveries; extraction holding time exceeded	NA	59 µg/L

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MEMORANDUM

DATE: February 10, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist PC
Sample Control Center

SUBJECT: Data Review Narrative for Pesticide Analyses for the Alaskan Cruise Ship Industry, Episode 6506

OVERVIEW

Under EPA Purchase Order EP-C-04-046, Pacific Analytical, Inc. (PAI) submitted data for the analysis of organohalide pesticides by EPA Method 1656A and organophosphorus pesticides by EPA Method 1657A for two samples in Episode 6506. Table 1 provides a list of the samples, matrices, description, and the required analytical methods.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Methods

EPA Sample #	Matrix	Sample Description	Sampling Date	Method
65800	Aqueous	SP3, Galley Wastewater	09/20/2004	1656A, 1657A
65900	Aqueous	SP11, Influent to Blackwater/Graywater Treatment System	09/20/2004	1656A, 1657A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Pesticide Analyses (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary tables (Tables 2A and 2B).

SUMMARY

All samples were successfully extracted and analyzed for the target analytes in EPA Methods 1656A and 1657A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks performed for each analysis detected no contamination above the laboratory's reporting limits. All organohalide pesticides samples were processed through gel permeation chromatography (GPC), and Florisil cleanup procedures. The laboratory also analyzed the samples for organohalide pesticides without Florisil cleanup. All organophosphorus pesticides samples were processed through GPC, and carbon column cleanup procedures. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable with the exception of the data issues described below. No matrix spike/matrix spike duplicate (MS/MSD) samples were required for this episode.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Reporting Limits

The laboratory's reporting limits are based on the lowest calibration points specified in the methods, adjusted for dilution, rather than the minimum levels (MLs) listed in the methods. In most cases, the laboratory's reporting limits are lower than the method-specified MLs.

Some sample results in this episode were reported by the laboratory with a "J" flag, which indicates an estimated result that is below the laboratory's reporting limit. In keeping with current EAD practices, and to maintain consistency, all "J" flagged data will be reported in the database as non-detects at the laboratory's reporting limits.

Multiple Qualifiers

Some analytical results were affected by multiple qualifiers. In cases where these qualifiers suggest different biases, SCC considers the data to be estimated values. The effect of each QC failure and its associated qualifier are described in this data review narrative. Where multiple QC failures occur, the cumulative effects of the associated qualifiers are documented in the Tables 2A and 2B.

DATA ISSUES: METHOD 1656A

Surrogate Recoveries

Two sets of data were submitted for this episode, for Florisil and non-Florisil cleanup fractions. For the Florisil cleanup fractions, all surrogate recoveries were below the method-specified criteria for samples 65800 and 65900. For the non-Florisil cleanup fractions, two out of three surrogate recoveries were below the method-specified criteria. The laboratory narrative states that the samples contained a great deal of surfactant and suspended particles. The chromatograms of the non-Florisil fraction show severe matrix interference in the samples. Therefore, SCC recommends reporting all results from the Florisil cleanup fraction in the database, and considers the data to be minimum values due to low surrogate recoveries. Please note that SCC did not initiate the reanalysis because the sample holding time had expired by more than 60 days. These cases are detailed in Table 2A.

Ongoing Precision and Recovery (OPR)

Alpha-BHC, metribuzin, 4,4'-DDT, dichlone, alpha-chlordane, norflurazon, and carbophenothion were recovered below the method-specified criteria in Florisil cleanup fraction, but had acceptable recoveries in non-Florisil cleanup fraction. The laboratory suggested using the results from non-Florisil fraction for these analytes. However, the chromatograms of the non-Florisil fraction show severe matrix interference, suggesting that a positive interference may be present in the actual samples. Therefore, SCC recommends reporting all results from Florisil cleanup fraction in the database, and considers the non-detected results for these analytes to be minimum values. These cases are detailed in Table 2A.

Sample Results

According to the method, the computed result for a target analyte detected on the primary column analysis must be confirmed and agree within a factor of two with the result computed for that analyte on the confirmation column. For sample 65900, diallate B and propachlor results from the primary column differed by more than the method-specified factor of two from the confirmation column. After discussions with SCC, EPA authorized the analysis of sample 65900 by a GC/MS method utilizing selected ion monitoring (SIM) to determine if the any target analytes were, in fact, present in the samples,

or if the original GC/ECD results were false positives. The results of the GC/MS SIM analysis were subsequently reviewed by SCC and none of these pesticides were confirmed for this sample.

DATA ISSUES: METHOD 1657A

Surrogate Recoveries

All surrogate recoveries were below the method-specified criteria for sample 65900. Therefore, SCC considers all non-detected results in sample 65900 to be minimum values (See Table 2B). Please note that SCC did not initiate the reanalysis because the sample holding time had expired by more than 60 days.

Ongoing Precision and Recovery (OPR)

The laboratory prepared and analyzed two OPR samples for this episode. Methamidophos was recovered below the method-specified criteria in both OPRs. Therefore, SCC considers the non-detected results for methamidophos in both samples to be minimum values (see Table 2B).

If you have any questions regarding the analyses of these samples or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments:

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

Table 2A
Data Review Summary Table

Episode: 6506 **Analysis:** 1656A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65800, 65900	All target analytes listed in M1656A,	Minimum values	Low surrogate recoveries	NA	ND
65800, 65900	alpha-BHC, metribuzin, 4,4'-DDT, dichlone, alpha-chlordane, norflurazon, and carbophenothion	Minimum values	Low surrogate recoveries and low OPR recoveries	NA	ND

ND = Non-detect at the laboratory's reporting limit. See level in the database.
NA = Not applicable

Table 2B
Data Review Summary Table

Episode: 6506 **Analysis:** 1657A

Industry: Alaskan Cruise Ship **Reviewer:** P. Chinyavong

Sample	Analyte	Action	Reason	SCC Qual	Level
65900	All target analytes listed in M1657A	Minimum values	Low surrogate recoveries	NA	ND
65900	methamidophos	Minimum values	Low surrogate recoveries and low OPR recoveries	NA	ND
65800	methamidophos	Minimum values	Low OPR recoveries	NA	ND

ND = Non-detect at the laboratory's reporting limit. See level in the database.
NA = Not applicable

Quality Assurance Review of Laboratory Data Collected From Large Cruise Ships in Alaska Waters

Sampling Episode 6506

Data Validation Report For Settleable Solids Samples

Prepared By:

Eastern Research Group
14555 Avion Parkway, Suite 200
Chantilly, Virginia 20151

February 10, 2005

Settleable Solids Method 160.5

Completeness

During Sampling Episode 6506 onboard the HAL Oosterdam, a total of 33 samples (excluding QC samples) were collected for analysis of settleable solids (SS) by EPA Method 160.5. Sample numbers ranged between 65792 and 66000. One sample from the food pulper vacuum tank could not be collected because this system was not operating during the sampling episode, resulting in a sampling completeness of 97% for this episode.

The data package submitted by the analytical laboratory, Analytica Alaska Southeast, contained complete SS data for all submitted samples, resulting in a laboratory completeness of 100%. A list of samples collected and analyzed during Sampling Episode 6506 is provided in Table 1.

Table 1. SS Samples Collected During Sampling Episode 6506

Sample Numbers	Sample Point Description
65792	Accommodations Wastewater
65796	Laundry Wastewater
65800	Galley Wastewater
65808	Food Pulper Centrifuge
65812, 65816, 65820, 65824, 65828	Influent to Graywater Treatment
65852, 65856, 65860, 65864, 65868, 65888	Effluent from Graywater Treatment
65896, 65900, 65904, 65908, 65912	Influent to Blackwater/Graywater Treatment
65936, 65940, 65944, 65948, 65952, 65956, 65972	Effluent from Blackwater/Graywater Treatment
65980, 65984, 65988, 65992, 65996	Final Combined Discharge
66000	Source Water

According to the Quality Assurance Project Plan (QAPP) developed for the Rulemaking Support for Large Cruise Ships in Alaska Waters, sampling completeness is the number of valid samples collected relative to the number of samples planned for collection; analytical completeness is the number of valid sample measurements relative to the number of valid samples collected; and overall completeness is the number of valid sample measurements relative to the number of samples planned for collection. For the cruise ship sampling program a minimum goal of 90% completeness for sampling and analytical completeness has been established, and a minimum goal of 81% for overall completeness (determined by multiplying

sampling and analytical completeness goals) has been established. For Sampling Episode 6506, overall completeness for SS was 97%.

Holding Times

Method 160.5 requires SS samples be analyzed within 48 hours following collection. Analysis of traffic reports and laboratory data sheets indicates all SS samples received by the laboratory were analyzed within the 48 hour holding time.

Precision Analysis

Reproducibility for SS is measured as relative percent difference (RPD) between duplicate samples. The QAPP for the Cruse Ship Rulemaking targets the RPD for all field duplicate samples as less than 30%. Field duplicate samples were collected for SS, and the results are shown in Table 2. The RPDs shown in Table 2 could not be calculated because all duplicate sample results were less than the laboratory reported detection limit. Although the RPD for these samples cannot be calculated, SS analysis precision is acceptable for this program, and the reported SS results are valid.

Table 2. Relative Percent Difference Between Field Duplicate Samples

Sample No.	SS Result	Sample No.	SS Result	RPD	RPD Target
65868	<0.11 ml/L	65888	<0.10 ml/L	NA	<30%
65936	<0.10 ml/L	65956	<0.13 ml/L	NA	<30%
65952	<0.10 ml/L	65972	<0.11 ml/L	NA	<30%

NA: RPD cannot be calculated since one or both of the sample results is less than the detection limit.
RPD target from QAPP for Rulemaking Support for Large Cruise Ships in Alaska Waters, May 2004

Data Quality Assessment

This data validation assessment indicates the SS data collected during Sampling Episode 6506 can be used for the large cruise ship rulemaking effort.

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MEMORANDUM

DATE: February 9, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Pornkeo Chinyavong, Quality Assurance Chemist
Sample Control Center

PC

SUBJECT: Data Review Narrative for PCB Congener Analyses for the Alaskan Cruise Ship Industry, Episode 6506

OVERVIEW

Under EPA Purchase Order EP-C-04-047, Axys Analytical Services submitted data for the analysis of chlorinated biphenyl congeners by EPA Method 1668A for one sample in Episode 6506. Table 1 provides a list of the sample, matrix, sample description, and the required analytical method.

Table 1 - Sample Identifiers, Descriptions, Sampling Dates, and Analysis Method

Episode	EPA Sample #	Matrix	Sample Description	Sampling Date	Method
6506	65896	Aqueous	SP11, Influent Black/Gray Water to Treatment System	9/19/04	1668A

These data have been reviewed in accordance with SCC's Data Review Guidelines for Chlorinated Biphenyl Analysis (November 2004). Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with this sample. Based on this review, all data in this episode are considered to be of acceptable quality.

SUMMARY

The sample was successfully extracted and analyzed for the target analytes in EPA Method 1668A within the method-specified holding times. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks associated with this sample detected no contamination above the laboratory's reporting limits. The QC samples, including the ongoing precision and recovery (OPR) sample, demonstrated that laboratory performance for these analyses was acceptable, with the clarification provided below.

Reporting Limits

The sample was extracted using a 897-mL aliquot, rather than the method-specified 1000-mL aliquot, due to volume constraints. This variation in sample size increased the minimum levels (MLs) for sample 65896 by 11%. The MLs provided in the database for this sample reflect the smaller sample volume.

Lock mass disturbance was observed in the initial analysis of sample 65896. The disturbance affected PCB-207 and PCB-208. The laboratory analyzed a 5-fold dilution of this sample's extract, and the results for PCB-207 and PCB-208 were reported from the 5-fold dilution. The MLs provided in the database for PCB-207 and PCB-208 for sample 65896 reflect the 5-fold dilution.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

If you have any questions regarding the analyses of this sample or the review of these data, please contact me, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC

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MEMORANDUM

DATE: February 10, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Sara Clark, Quality Assurance Chemist
Sample Control Center

SUBJECT: Data Review Narrative for Available Cyanide Analyses by Method OIA-1677 for the Alaskan Cruise Ship Industry, Episode 6506

OVERVIEW

Under EPA Purchase Order EP-C-04-048, Bayer Material Science LLC, submitted data for the analyses of available cyanide by EPA Method OIA-1677 for 32 aqueous samples and 4 solid samples in Episode 6506. Table 1 provides a listing of samples, matrices, sample identifiers, descriptions and sampling dates. Available cyanide was the only analysis performed by Bayer for these samples.

Table 1 - Sample Identifiers, Matrices, Descriptions, and Sampling Dates

EPA Sample #	Matrix	Sample Description	Sampling Date
65792	Aqueous	SP1, Accommodations	09/21/04
65796	Aqueous	SP2, Laundry WW	09/19/04
65800	Aqueous	SP3, Galley WW	09/20/04
65808	Solid	SP5, Food pulper WW	09/22/04
65812	Aqueous	SP6, Influent to GW TS	09/19/04
65816	Aqueous	SP6, Influent to GW TS	09/20/04
65820	Aqueous	SP6, Influent to GW TS	09/21/04
65824	Aqueous	SP6, Influent to GW TS	09/22/04
65828	Aqueous	SP6, Influent to GW TS	09/23/04
65852	Aqueous	SP8, Effluent from GW TS	09/19/04
65856	Aqueous	SP8, Effluent from GW TS	09/20/04
65860	Aqueous	SP8, Effluent from GW TS	09/21/04
65864	Aqueous	SP8, Effluent from GW TS	09/22/04
65868	Aqueous	SP8, Effluent from GW TS	09/23/04
65872	Aqueous	SP9, Effluent from GW TS	09/23/04
65880	Aqueous	SP9, Effluent from GW TS	09/22/04

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Table 1 - Sample Identifiers, Matrices, Descriptions, and Sampling Dates

EPA Sample #	Matrix	Sample Description	Sampling Date
65896	Aqueous	SP11, Influent to BW/GW TS	09/19/04
65900	Aqueous	SP11, Influent to BW/GW TS	09/20/04
65904	Aqueous	SP11, Influent to BW/GW TS	09/21/04
65908	Aqueous	SP11, Influent to BW/GW TS	09/22/04
65912	Aqueous	SP11, Influent to BW GW TS	09/23/04
65936	Aqueous	SP13, Effluent BW/GW TS	09/19/04
65940	Aqueous	SP13, Blackwater effluent	09/20/04
65944	Aqueous	SP13, Effluent BW/GW TS	09/21/04
65948	Aqueous	SP13, Effluent BW/GW TS	09/22/04
65952	Aqueous	SP13, Effluent from BW/GW TS	09/23/04
65956	Aqueous	SP14, Effluent from BW/GW TS	09/19/04
65976	Solid	SP15, GW SWECO solids	09/20/04
65980	Aqueous	SP16, Combined discharge	09/19/04
65984	Aqueous	SP16, Combined discharge	09/20/04
65988	Aqueous	SP16, Combined discharge	09/21/04
65992	Aqueous	SP16, Combined discharge	09/22/04
65996	Aqueous	SP16, Combined discharge	09/23/04
66000	Aqueous	SP17, Source water	09/20/04
66009	Solid	SP20, BW/GW SWECO solids	09/21/04
66010	Solid	SP21 GW/BW biosludge	09/21/04

These data have been reviewed in accordance with SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), and with the specifications listed in the analytical requirements summary for this episode. Below is a summary of the results of the data review process, followed by detailed descriptions of data issues identified with these samples. Based on this review, all data in this episode are considered to be of acceptable quality with the qualifications described below and detailed in the attached data review summary table (Table 2).

SUMMARY

All samples were successfully analyzed within the method-specified holding times for available cyanide. Initial precision and recovery samples (IPRs) were successfully performed prior to sample analysis. The calibration and continuing calibration standards were successfully analyzed. Preparation blanks were performed and there was no contamination detected above the laboratory reporting limits. The QC samples, including the ongoing and precision recovery sample (OPR) and matrix spike/matrix spike

duplicate (MS/MSD) samples, demonstrated that laboratory performance for these analyses were acceptable, with the exception of the data issues described below.

DATA ISSUES: AVAILABLE CYANIDE GREATER THAN TOTAL CYANIDE

Sample Results

For all samples in this episode, SCC evaluated total cyanide results against available cyanide results, and found that available cyanide was detected in samples 65896, 65900, 65904, 65908, and 65912 while total cyanide were not detected in these samples. In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. However, for these samples, it is important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the available cyanide determination was performed by a different laboratory. In addition, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results. Therefore, it may not be possible to identify problems that would invalidate one cyanide fraction or the other.

A comparison of the total cyanide results and available cyanide results for samples 65896, 65900, 65904, 65908, and 65912 indicates that the total cyanide results were non-detects at 5 μg/L, while available cyanide was detected in each of these samples at levels from approximately 36 to 77 μg/L.

All five of these samples are from the same sampling point, SP 11, and represent influents to the black water and gray water treatment system. Thus, these samples are not treated effluents. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65896, 65900, 65904, 65908, and 65912 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6506, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Please note that the samples were analyzed for total cyanide by Prochem (formerly QBiochem). A separate narrative has been prepared for the total cyanide analysis.

If you have any questions regarding the analyses of these samples or the review of these data, please contact SCC's Data Review Team Leader, Pornkeo Chinyavong, by telephone at (703) 461-2346 or by facsimile at (703) 461-8056.

Attachments

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Harry McCarty, CSC
Pornkeo Chinyavong, CSC

Table 2
Data Review Summary Table

Episode: 6506 **Analysis:** Available Cyanide

Industry: Alaska Cruise Ship **Reviewer:** S. Clark

Sample	Analyte	Action	Reason	SCC Qual	Level
65896, 65900, 65904, 65908, 65912	Available cyanide	—	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.	IRR	NA

NA = Not applicable
IRR = Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: January 18, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty
Senior Scientist

SUBJECT: Issues Associated with Results for Total Cyanide versus Available Cyanide for Episodes 6503, 6504, 6505, and 6506

The purpose of this memorandum is to provide a general discussion of the analysis of various forms of cyanide in aqueous samples, describe the cyanide analyses conducted as part of EPA's investigation of discharges from Alaskan cruise ships, and provide recommendations regarding specific results from Sampling Episodes 6503, 6504, 6505, and 6506.

Forms of Cyanide

Cyanide is an inorganic moiety composed of one carbon atom and one nitrogen atom that is most often found as an anion with a charge of -1. The cyanide anion can bond with various metals or other elements to form a wide range of cyanide compounds. The simplest form of cyanide is hydrogen cyanide, HCN, which readily dissociates into H^+ and CN^- in water. HCN is known as "free cyanide" and is the most toxic form of cyanide. Most forms of cyanide are toxic, with their toxicities depending on their ability to release free cyanide.

"Total cyanide" (or "cyanide, total") is an operationally defined term used to describe the cyanides that are measured using the total cyanide test. Total cyanide methods attempt to measure the amount of CN^- present in a sample, regardless of its oxidation state or complexation to other ions or compounds. Some complexes and organic cyanide compounds are resistant to the dissociation that occurs during the digestion/distillation step, and others are completely decomposed. Therefore, total cyanide is a method-defined parameter because the analytical conditions determine the actual analyte quantity measured.

Compounds such as metallocyanides are resistant to oxidation, with iron cyanide being one of the most resistant, and nickel, copper, and noble metal cyanides being somewhat resistant. These compounds will contribute to the measured total cyanide to some degree, but are not always completely recovered by the digestion/distillation procedure. Cyanide compounds such as thiocyanate, cobaltocyanide compounds, and cyanohydrin organic compounds are not measured at all by this procedure include because they decompose during the digestion procedure.

Two other operationally defined groups of cyanide species are "available cyanide," and "cyanide amenable to chlorination" (or "amenable cyanide"). Available cyanide generally encompasses both the free cyanide and those complexed species that are relatively easily dissociated in a weak acid solution. Amenable cyanide is the term used to describe that fraction of cyanide that can be destroyed by the common wastewater treatment procedure of chlorinating the wastewater. Some cyanides in solution will react with chlorine (Cl_2) to form cyanogen chloride (CNCl), a highly toxic gas with limited solubility. The cyanogen chloride hydrolyzes at alkaline pH to form the cyanate ion (CNO^-), which is much less toxic than the parent cyanide. Amenable cyanide encompasses the true free cyanide portion, plus additional cyanides that easily dissociate in aqueous solutions.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Analytical Methods for the Analysis of Cyanide in Aqueous Samples

Total Cyanide Methods

The seven methods approved at 40 CFR 136 for total cyanide in aqueous samples are:

- EPA Method 335.2
- EPA Method 335.3
- Standard Method 4500-CN^- D
- Standard Method 4500-CN^- E
- ASTM Method D2036-98A
- USGS Method I-3300-85
- USGS Method I-4302-85

EPA Methods 335.2 and 335.3 were employed by the two laboratories that analyzed samples from Episodes 6503, 6504, 6505, and 6506 for total cyanide. However, this general discussion applies to all seven approved methods.

All of the total cyanide methods involve digestion of the sample using concentrated sulfuric acid with magnesium ion in solution as a catalyst. (The digestion procedure is presented as the stand-alone procedure Standard Method 4500-CN^- C). The cyanide is converted to HCN gas, which is collected in a scrubber containing NaOH. This solution is then analyzed for the CN^- ion. The determinative methods use one of several techniques to measure CN^-, including titration with silver nitrate, colorimetry with an organic dye, or automated distillation-colorimetry for continuous flow analytical systems that utilizes UV oxidation of the sample to release bound cyanide.

Available Cyanide Methods

The four methods approved at 40 CFR 136 for available cyanide in aqueous samples are:

- EPA Method 335.1
- Standard Method 4500-CN^- G
- ASTM Method D2036-98B
- Method OIA-1677

Method OIA-1667 was employed for the analyses of available cyanide in Episodes 6503, 6504, 6505, and 6506. However, this general discussion applies to all four approved methods.

Although these four methods are approved at 40 CFR 136 for “available cyanide,” there are slight differences in forms of cyanide that are targeted by these methods. Generally speaking, the differences are not significant in compliance monitoring, but may be more important in other types of investigations.

The OIA-1677 procedure targets the weak acid dissociable cyanide by treating the sample with ligand-exchange reagents that release cyanide ions from the metal-cyano complexes. During the analysis, cyanide ions are converted to hydrogen cyanide (HCN) that passes through a gas diffusion membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically, using a silver electrode.

EPA Method 335.1, SM 4500-CN^- G, and ASTM D2036-98B measure the cyanide amenable to chlorination. In these methods, two aliquots of the sample are analyzed. One aliquot is subjected to chlorination and the other aliquot is not. Both aliquots are distilled and analyzed for CN^-. The amenable

cyanide is calculated as the difference between the cyanide results from the chlorinated and nonchlorinated aliquots.

Difficulties and Interferences in the Analysis of Cyanide

A number of interferences affect cyanide determinations. Strong oxidizers, such as free chlorine, will destroy the "amenable" portion of cyanide. Sulfide present in the sample will oxidize cyanide into thiocyanate, which is not measurable in the cyanide methods. The sample should be tested for sulfide at the time of sample collection, and if sulfides are found, they should be removed by precipitation with lead carbonate or cadmium nitrate. This precipitation procedure should take place before the sample is preserved with NaOH, and any insoluble sulfide that is produced should be removed by filtration. Additional steps may be needed if the sample contains sulfide *and* particulate matter that may consist of alkali metal-heavy metal-cyanide complexes.

Most interferences in the total cyanide determination are removed by the distillation step, but some are not. Nitrate and nitrite can form cyanide as a reduction product of nitrogen-containing organic compounds, and are removed by the addition of sulfamic acid during distillation. Aldehydes can form cyanohydrins, which will convert to nitrile during the digestion. Sulfides also can be produced during distillation, and will distill along with cyanide and form thiocyanate. Sulfide production can be prevented by the addition of lead carbonate to the absorber solution, and the subsequent filtration of the absorber solution before analysis. Other potential interferences include sugars that can form cyanohydrins, sulfur compounds that may release sulfide, compounds that could release or form nitrite, as well as any sample constituent that could produce one of the interferences under the conditions of the digestion.

Method OIA-1677 does not employ a digestion step. Therefore, sulfides must be removed by the precipitation procedure described above. In addition to concerns about sulfides reacting with the cyanide in the sample before it can be measured (i.e., a negative interference), sulfides also can be a positive interference in this procedure if they react with acid in the sample to produce hydrogen sulfide (HS_2). The hydrogen sulfide will cross the membrane in the gas diffusion cell and produce a signal at the silver electrode that would be measured as cyanide. As noted in the method, "polysulfides" (compounds containing more than one sulfide) can be intractable interferences.

Interpretation of Cyanide Results

In theory, the total cyanide results in any given sample will be greater than either the free or available cyanide results for the same sample. While this usually holds true for wastewater effluent samples, some effluents and some other sample types, such as influents, may yield results in which the free or available cyanide results exceed the total cyanide results. For example, the results for free cyanide derived using the chlorination technique can result in free cyanide concentrations greatly in excess of total cyanide concentrations. When this occurs, it is likely due to the formation of cyanide by chlorination of nitrogen-containing organic compounds in the sample. While it might be possible to determine if such nitrogen-containing organics were present in the sample, this step is neither required nor practical for laboratories performing routine cyanide analyses.

Sulfides that may be in the sample present a significant possibility for false negative results for total cyanide through the oxidization of cyanide to thiocyanate, which is not measured by the cyanide methods, as discussed above. Sulfides can be both a negative interference and a positive interference with the determination of available cyanide by Method OIA-1677, as described above.

It is also important to recognize that the total cyanide is determined using a separate sample from that used for free or available cyanide, and that the amenable cyanide determination is made using

separate aliquots of a separate sample. Thus, the overall homogeneity of the waste stream being sampled can have a significant effect on the cyanide results.

While the results for any cyanide measurement are evaluated by SCC relative to the requirements of the methods used for the determinations, it may not be possible to identify problems that would invalidate one cyanide fraction or the other. In instances where there are one or more QC failures associated with one of the cyanide fractions, but not with the other fraction, the results for the fraction with the QC failures will be appropriately qualified.

In instances where there are no QC failures associated with either cyanide fraction, but the available cyanide results are greater than the total cyanide results by a large margin, there is no way to determine which analysis was correct. In such cases, both sets of cyanide results are suspect. For the purposes of reviewing results for EPA's Effluent Guidelines Program, when cyanide is reported as present (e.g., not a non-detect) in both fractions and there are no QC failures in either fraction, differences where the available cyanide results are more than 30% above the total cyanide results suggest that irreconcilable problems exist. The 30% difference is a consensus value used by SCC. Differences less than 30% are considered a function of the routine variability that could be present in both measurements.

When such irreconcilable problems exist with the results of paired samples analyzed for both total and available cyanide, SCC recommends that both results (total and available) be included in the database, and that both results be flagged to alert the data user to the presence of such problems.

Cyanide Methods Used for Samples from the Alaskan Cruise Ship Project

The following table lists the methods used for total and available cyanide for Episodes 6503, 6504, 6505, and 6506. Two different laboratories performed the total cyanide analyses for these four episodes, using two different methods approved at 40 CFR 136. One other laboratory analyzed the available cyanide for all four episodes using Method OIA-1677.

Episode #	Method for Total Cyanide	Method for Available Cyanide
6503	EPA Method 335.3	Method OIA-1677
6504	EPA Method 335.2	Method OIA-1677
6505	EPA Method 335.3	Method OIA-1677
6506	EPA Method 335.2	Method OIA-1677

Based on communications with the sampling contractor, the samples were tested for sulfide in the field, using a field colorimeter with a detection limit of approximately 10 µg/L. Samples testing positive for sulfides were treated in the field to minimize the interferences. Because of concerns regarding whether the treated samples were subsequently filtered in the field, the laboratories were instructed to filter any sample showing turbidity.

A review of the traffic reports (TRs) for the samples in these four episodes indicates that some of the samples in Episode 6503, the first episode in the Alaskan Cruise Ship project, were not treated with lead carbonate to remove sulfides. SCC consulted EPA and the sampling contractor and determined that the following 11 samples were not treated with lead carbonate:

65202, 65207, 65211, 65227, 65231, 65235, 65269, 65273, 65277, 65283, and 65295

In an effort to address the potential positive interference of nitrate and nitrite in the samples, the laboratories performing the total cyanide analyses were advised to increase the amount of sulfamic acid added to each sample during distillation by a factor of 2, from 2 g per sample to 4 g per sample.

Episode-specific Findings

SCC has reviewed the results for both total cyanide and available cyanide in Episodes 6503, 6504, 6505, and 6506. Episode-specific findings are detailed below.

In addition to the data qualifiers described in SCC's *Data Review Guidelines for Classical Wet Chemistry Analyses* (November 2004), two additional qualifiers were developed to address the total and available cyanide results from the Alaskan Cruise Ship Project. In cases where the available cyanide results exceed those for total cyanide by more than 30% and there are not any matrix-specific quality control data such as matrix spike recoveries, the total cyanide and available cyanide results will be flagged with the "IRR" qualifier. The "SCC Reason" field in the database for such results will read "Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose."

In other instances, when SCC's review identifies multiple concerns with the results for a given sample, including those that begin with sample collection and others involving the analysis of the sample itself or any associated quality control samples, the total cyanide and available cyanide results will be flagged with the "MISCA" qualifier. The "SCC Reason" field in the database for such results will read "Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample."

Episode 6503

Three sets of matrix spike/matrix spike duplicate (MS/MSD) samples were prepared for total cyanide analysis in Episode 6503 on samples 65207 (accommodations wastewater), 65269 (an effluent), and 65273 (an effluent). The MS/MSD recoveries for the three aqueous MS/MSD pairs were below the acceptance limits:

- 22% and 21% for sample 65207,
- 30% and 33% for sample 65269, and
- 5% and 1% for sample 65273

suggesting a potential for low bias in the total cyanide results for the associated aqueous samples.

The recoveries for the laboratory control samples (LCS, OPR, or QC check sample) analyzed along with the field samples were acceptable, indicating that the laboratory's overall analytical process was in control and suggesting either problems with the distillation process or an interference present in the sample matrix. Because the focus of the EAD analytical contracts is on effluent samples and because there are no acceptance criteria for aqueous matrices other than effluents, no MS/MSD analyses were performed on samples representing influents to the treatment process.

The total cyanide result for Sample 65273 (effluent) was reported as a non-detect at 5 µg/L and available cyanide was a non-detect at 2 µg/L. An MS/MSD pair for available cyanide was prepared from this sample and had recoveries of 101% and 102% respectively, while the MS/MSD recoveries for total cyanide were 5% and 1%, as noted earlier. This suggests a significant potential for low bias in the total cyanide result. Therefore, based on the low MS/MSD recoveries for total cyanide in this sample, the total

cyanide non-detect is considered a minimum value and the available cyanide result is considered acceptable without qualification.

There were nine other samples in Episode 6503 that exhibited the pattern of total cyanide results less than the available cyanide results. Samples 65219, 65227, 65231, and 65235 are influents to treatment and, as noted above, there are no MS/MSD analyses that demonstrate the performance of either method for this matrix type. Samples 65227, 65231, and 65235 also are among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and given the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for samples 65227, 65231, and 65235 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples. Sample 65219 was treated in the field, therefore SCC recommends including both cyanide results for sample 65219 in the database, but flagging them to indicate the irreconcilable differences.

The total cyanide results for Sample 65207 (accommodations wastewater) were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 15.7 µg/L. The MS/MSD recoveries for total cyanide were 21% and 22%, as noted earlier. Sample 65207 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, given the low MS/MSD recoveries for total cyanide in this sample and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65207 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65211 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Total cyanide was detected at 14 µg/L, while available cyanide was reported at 88.4 µg/L. Sample 65211 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Therefore, lacking matrix-specific supporting data that might explain the observed differences, and the potential for positive interferences in the available cyanide measurements, SCC recommends flagging both cyanide results for sample 65211 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in this sample.

Sample 65295 is listed as a source water sample, a matrix type that should not present significant analytical difficulties. Sulfide was not detected in this sample by the field test performed at the time of collection and therefore, this sample is among the 11 samples that were not treated with lead carbonate. Although the presence of available cyanide at 19 µg/L in the source water is unexpected, there is no analytical evidence to suggest that the available cyanide result be excluded. However, an engineering review or other information not available to SCC may lead to a different conclusion. Therefore, SCC recommends including both cyanide results for sample 65295 in the database, but flagging them to indicate the irreconcilable differences.

Episode 6503 included two sets of field duplicate samples that were sent to the laboratories blind. The two pairs were samples 65261 and 65281, and samples 65265 and 65283, all effluent samples. The total cyanide results in sample 65261 were reported as a non-detect at 5 µg/L, while available cyanide was reported as a non-detect at 2 µg/L. For sample 65281, the blind field duplicate, the total cyanide results were reported as a non-detect at 5 µg/L, while available cyanide was detected in this sample at 8.96 µg/L. A similar pattern occurs for the cyanide results in the other field duplicate pair. Total cyanide was reported as a non-detect at 5 µg/L in both samples 65265 and 65283, while available cyanide was detected at 5.86 µg/L in sample 65265 and as a non-detect a 2 µg/L in sample 65283.

The MS/MSD recoveries for total cyanide in effluent sample 65273 were very low (1% and 5%), and low (33% and 30%) in sample 65269, suggesting a potential negative basis that may affect the total cyanide results in samples 65261, 65281, 65265, and 65283. Therefore, SCC recommends that the total cyanide results in sample 65261 and 65281 be considered minimum values. The difference between the available cyanide results in the two field duplicate samples (e.g., a non-detect at 2 µg/L and a detect at 8.96 µg/L) cannot be explained on the basis of the MS/MSD results for available cyanide in sample 65273, which was also an effluent. Given the discrepancy between the field duplicate results for available cyanide, SCC recommends including the available cyanide results for samples 65261 and 65281 in the database, but flagging them to indicate the irreconcilable differences. SCC recommends that the total cyanide results for samples 65261 and 65281 also be flagged to indicate the irreconcilable differences, as a further precaution.

Because of the low MS/MSD recoveries in the other effluent samples, the total cyanide result for sample 65265 is considered a minimum value. The available cyanide result of 5.86 µg/L is well within 30% of the reported detection limit for total cyanide (e.g., 5 µg/L), and therefore would normally not be qualified. However, because the available cyanide result in the field duplicate of the sample, 65283 is a non-detect at 2 µg/L, SCC recommends including both the total and available cyanide results for sample 65265 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65283 also is among the 11 samples in this episode that were not treated with lead carbonate in the field to remove sulfides. Given the very low MS/MSD recoveries for total cyanide in effluent samples in this episode, SCC recommends flagging both cyanide results for sample 65283 in the database to indicate that there are multiple issues with sample collection and analysis that may have led to the irreconcilable results observed in these samples.

Episode 6504

Three sets of MS/MSD samples were prepared for total cyanide analysis in Episode 6504 on samples 65519 (an effluent), 65523 (an effluent), and 65527 (accommodations wastewater), and all showed acceptable spike recoveries. Thus, there do not appear to be pervasive problems with the recovery of total cyanide in samples from this episode.

A comparison of the total cyanide results and available cyanide results for samples 65395, 65455, 65459, 65463, 65467, and 65471 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at approximately 11 to 36 µg/L. In addition, total cyanide was reported as present in sample 65411 at 6 µg/L, while the available cyanide result was 35.7 µg/L (e.g., six time the total cyanide result).

Sample 65395 is listed as the galley wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65395 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65411 is listed as the food pulper wastewater. This description suggests that this matrix is not a treated effluent, but may be a component of the influent to the treatment system, and as noted above, there are no MS/MSD data that demonstrate method performance for matrices other than effluents. During the review of the data, SCC noted that the traffic report for the aliquot of Sample 65411 for total cyanide analysis indicated that the aliquot was collected at 14:00 on 8/10/04, while the traffic report for the aliquot submitted for available cyanide analysis indicated that that aliquot was collected at 3:00 PM (15:00) on 8/11/04. This concern was resolved following discussions with EPA and the sampling contractor, whose field records indicated that both aliquots were collected at the same time, and that the

one traffic report was incorrect. Having resolved the issue of the time of sample collection, but lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65411 in the database, but flagging them to indicate the irreconcilable differences.

Samples 65455, 65459, 65463, 65467, and 65471 are all influents to treatment, collected from the same sampling point on consecutive days. The results from samples 65463, 65467, and 65471 are remarkably consistent, varying by only 0.2 µg/L across all three samples. The results for samples 65455 and 65459 are similar to one another, but about twice the concentrations found in the other three samples from this sampling point. There are no MS/MSD analyses that demonstrate method performance for this matrix type, but the consistency in the results suggests that whatever matrix effects may be taking place, they are reproducible. However, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65455, 65459, 65463, 65467, and 65471 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6504, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6505

The data for total cyanide samples in Episode 6505 were delivered in five separate data packages, each with its own associated QC sample results. Six pairs of MS/MSD samples were prepared for total cyanide analyses in Episode 6505 on samples 65603 (galley wastewater), 65635 (accommodations wastewater), 65711 (an effluent), 65715 (an effluent), 65719 (an effluent), and 65741 (screening solids).

The data for a seventh pair of MS/MSD samples were delivered in the data package with the results for samples 65731 (galley wastewater) and 65745 (biosolids). However, because of limitations on the sample volume that was provided to the laboratory, the MS/MSD samples were prepared from a non-EPA sample of indeterminate origin and therefore are not useful in evaluating the performance of the total cyanide method on cruise ship samples.

Three of the MS/MSD pairs for aqueous samples and the one MS/MSD pair for the solid samples had acceptable recoveries of total cyanide. None of the samples used to prepare MS/MSD aliquots were samples where the available cyanide results exceeded the total cyanide results.

The MS/MSD results for sample 65603 (galley wastewater) showed recoveries of 59% in both aliquots, which is below the acceptance limits, and suggests a potential low bias in the total cyanide result for that sample. The available cyanide result of 2.2 µg/L is below the detection limit for the total cyanide analysis. Therefore, SCC recommends qualifying the total cyanide result as a minimum value and accepting the available cyanide result as reported.

Although MS/MSD samples were prepared from sample 65741 (screening solids) and met the acceptance criteria, there are no MS/MSD results for the biosolids matrix in this episode. This limits SCC's ability to evaluate the potential effects of the sample matrix for sample 65745 (biosolids), where the available cyanide results are almost 40% higher than the total cyanide results. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65745 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65731 is a galley wastewater. The only MS/MSD results for galley wastewater in this episode are for sample 65603, where the recoveries were below the acceptance criteria. Given the

potential for low bias in this matrix, SCC recommends qualifying the total cyanide result as a minimum value. SCC recommends including both cyanide results for sample 65731 in the database, but flagging them to indicate the irreconcilable differences.

Sample 65659 is an influent sample and MS/MSD aliquots are not prepared for influents, as discussed earlier. Total cyanide was reported as not detected and the available cyanide was reported at 6 times the total cyanide detection limit. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for sample 65659 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6505, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Episode 6506

A comparison of the total cyanide results and available cyanide results for samples 65896, 65900, 65904, 65908, and 65912 indicates that the total cyanide results were non-detects at 5 µg/L, while available cyanide was detected in each of these samples at levels from approximately 36 to 77 µg/L.

All five of these samples are from the same sampling point, SP 2, and represent influents to the black water and gray water treatment system. Thus, these samples are not treated effluents. Therefore, lacking matrix-specific supporting data that might explain the observed differences, SCC recommends including both cyanide results for samples 65896, 65900, 65904, 65908, and 65912 in the database, but flagging them to indicate the irreconcilable differences.

Although there were three pairs of field duplicates collected for cyanide samples in Episode 6506, they all involved effluent samples, none of which showed disparate results between total and available cyanide.

Summary of Results from Episodes 6503, 6504, 6505, and 6506

SCC's recommendations for handling the total and available cyanide results for the Alaskan Cruise Ship project samples are summarized in the table on the following page

Note: The results in the database are reported in the units provided by the laboratories that performed the analyses. Method OIA-1677 specifies reporting results in units of micrograms per liter (µg/L), whereas the older methods (335.2 and 335.3) specify reporting results in units of milligrams per liter (mg/L). However, for ease of comparison in the table the follows, the results for total cyanide have been converted to the same units as the available cyanide results, µg/L. "ND" indicates that cyanide was not detected. In these cases, the reported detection limit is shown in parentheses.

If you have any questions about the information in this memorandum or the cyanide results in the database, please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Jodi King, ERG
Deb Falatko, ERG
Deb Miller, CSC
Michael Walsh, CSC
Pornkeo Chinyavong, CSC

Summary of SCC Recommendations for Cyanide Results in the Alaskan Cruise Ship Project

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65207	Accommodations wastewater	ND (5)	15.7	Sample not treated with lead carbonate to remove sulfides. Low MS/MSD recoveries for total cyanide. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65211	Food pulper wastewater	14	88.4	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65219	Influent to treatment	ND (5)	10.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65227	Influent to treatment	ND (5)	7.54	Samples not treated with lead carbonate to remove sulfides. No matrix-specific performance data for influents. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.
6503	65231		ND (5)	35.4	
6503	65235		ND (5)	16	
6503	65261	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65265		ND (5)	5.86	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65273		ND (5)	ND (2)	Total cyanide qualified as minimum value.
6503	65281		ND (5)	8.96	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6503	65283	Effluent from treatment	ND (5)	ND (2)	Total cyanide qualified as minimum value. Sample not treated with lead carbonate to remove sulfides. Multiple issues with sample collection and analysis that may have led to the irreconcilable results for total and available cyanide observed in this sample.

Episode	Sample #	Matrix	Total Cyanide (µg/L)	Available Cyanide (µg/L)	SCC Recommendation
6503	65295	Source water	ND (5)	19.1	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65395	Galley wastewater	ND (5)	22.4	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6504	65411	Food pulper	6	35.7	
6504	65455	Influent to treatment	ND (5)	26.9	
6504	65459	Influent to treatment	ND (5)	29	
6504	65463	Influent to treatment	ND (5)	11.7	
6504	65467	Influent to treatment	ND (5)	11.5	
6504	65471	Influent to treatment	ND (5)	11.6	
6505	65603	Galley wastewater	ND (5)	2.2	Total cyanide qualified as minimum value
6505	65659	Influent to treatment	ND (5)	30.7	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65731	Galley wastewater	ND (5)	12.9	Total cyanide qualified as minimum value. Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6505	65745	Biosolids	11	15.2	Irreconcilable results for total and available cyanide. Results may not be suitable for the intended purpose.
6506	65896	Influent to treatment	ND (5)	45.5	
6506	65900	Influent to treatment	ND (5)	36.2	
6506	65904	Influent to treatment	ND (5)	75.6	
6506	65908	Influent to treatment	ND (5)	72.2	
6506	65912	Influent to treatment	ND (5)	76.5	

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MEMORANDUM

DATE: January 31, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty, Ph.D.
Senior Scientist

SUBJECT: Summary of Telephone Conversation with the Available Cyanide Laboratory

At your suggestion, I contacted the laboratory that ran the available cyanide analyses for Episodes 6503 to 6506 and asked about cross-contamination concerns, glassware washing procedures, and other aspects of the analysis that might explain the discrepancies between the total and available cyanide results. I spoke with John Sebroski, the laboratory director at Bayer Material Science on January 19, 2005. John gave me the following information:

- All of the "glassware" involved in the analysis is disposable. This includes the cups on the autosampler, the tubing on the flow injection system, etc. They do not reuse any of it, so there are no washing issues.

- The design of the flow injection instrumentation minimizes any concerns about carryover because the sample is injected into a continuous flow of solution that runs through the analyzer.

- They do run frequent blanks on the instrument, especially after QC samples such as the lab control sample (LCS or OPR). Those QC samples are run at relatively high levels, and there is no evidence of carryover or memory effects in the blanks. (I also confirmed this prior to calling him, using the data for these four episodes.)

- The OIA-1677 method has an ASTM counterpart that uses the same technique. There is a 2004 version of the ASTM standard that addresses the potential for sulfide interferences by introducing a bismuth nitrate reagent into the system to remove sulfides. John indicated that the use of the bismuth nitrate reagent could easily be accommodated using Method OIA-1677, since the instrumentation is the same as the ASTM standard.

- John indicated that sulfide problems for total cyanide are always a significant issue. He also said that the flow injection system for available cyanide can detect (and be affected by) sulfides at a much lower level than the field test methods will detect. Therefore, any sample not treated with lead carbonate in the field may well have an interference for available cyanide, even if the field test was negative for sulfides.

In summary, my conversation with Mr. Sebroski confirms much of the information SCC summarized in our lengthy discussion of the issues surrounding the total and available cyanide results for this project and generally rules out the chance that analytical concerns, such as carryover or glassware cleaning procedures, as an explanation for the observed cyanide results. Please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com, if you have any questions.

Federal Sector
Civil Systems Development Division
6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

Computer Sciences Corporation
www.csc.com

MEMORANDUM

DATE: March 22, 2005

TO: Don Anderson, Project Officer
EPA EAD

FROM: Harry B. McCarty
Senior Scientist

SUBJECT: Further Examination of Ammonia Data for Episodes 6503 to 6506

At EPA's request, SCC performed additional reviews of the ammonia data for Episodes 6503 through 6506 for the Alaskan Cruise Ship project. The root of EPA's concern is an apparent discrepancy between the ammonia results for samples in Episodes 6503 and 6505 versus the results for samples from similar sampling points in Episodes 6504 and 6506.

SCC re-examined the results and raw data submitted by ALSI for Episodes 6503 and 6505 and the results and raw data submitted by ProChem for Episodes 6504 and 6506. SCC staff re-examined all of the sample shipping and custody records, looking for any discrepancies. SCC staff also contacted both laboratories and asked about potential problems with the ammonia analyses for these samples.

The results of this investigation confirm our original data review results, namely, there are no manifest errors in the data. The quality control (QC) results from each laboratory support the results provided and do not suggest any pervasive problems with the analyses (i.e., matrix spike recoveries and OPR results were well within the acceptance limits, blanks were free of ammonia at the levels of interest).

Both laboratories used the distillation procedure in EPA Method 350.2 to prepare the samples for the determinative analysis. Method 350.2 discusses the use of "microdistillation" glassware in place of the larger glassware in the method. Both laboratories employed microdistillation glassware, with ALSI using a 150-mL initial sample volume and ProChem using a 100-mL volume.

The laboratories used different determinative methods for ammonia. ALSI used EPA Method 350.1, an automated colorimetric method, whereas ProChem used EPA Method 350.3, an ion selective electrode procedure. Both methods are approved for ammonia analysis at 40 CFR 136. Method 350.1 has a much narrower dynamic range than Method 350.3 (0.01 to 2 mg/L versus 0.05 to 1400 mg/L). As a result, ALSI had to analyze many of the samples at dilutions of 10 - 100x, while ProChem did not have to dilute many of the samples. SCC examined the blank data from both laboratories and there is no evidence that the reagent water used to prepare blanks and to dilute samples would have contributed to the sample results for ammonia. SCC reviewed the reporting limits used by both laboratories relative to the capabilities of the methods. As noted above, the dynamic range of Method 350.1 is five times lower than that of Method 350.3, however the samples from this project were generally not at such low levels. Therefore, there is no evidence that method sensitivity or reporting practices resulted in the discrepancies of concern to EPA.

It is important to note that the two laboratories never analyzed aliquots of the same samples, so there is no direct means of comparing their results.

6101 Stevenson Avenue
Alexandria, Virginia 22304
703.461.2000 Fax 703.461.2020

In summary, SCC's examination of the data did not provide any explanation for the differences in the results for ammonia from these two laboratories. Although the laboratories used different methods for the determinative analyses, both methods are approved at 40 CFR 136 and both methods are applicable to the samples for this project. This review was limited to the analytical data provided by the laboratories and SCC cannot rule out the possibility that differences in sampling, sample handling prior to arrival at the laboratories, or in the waste collection and treatment systems among the cruise ships affected the samples analyzed by the two laboratories.

If you have any questions about the information in this memorandum or the ammonia results in the database, please do not hesitate to contact me at 703-461-2392, or by email at hmccarty@csc.com.

cc: Beverly Randolph, EPA
Marla Smith, EPA
Nelson Andrews, EPA
Deb Falatko, ERG
Jodi King, ERG
Deb Miller, CSC
Erin Salo, CSC
Michael Walsh, CSC